

SERIAL NO. 09/331,729

ATTORNEY L. CHECKET NO. 1996/F 364

1756

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In re Application of: Osan *et al.*

Serial No. 09/331,729

Filing Date: August 26, 1999

For: Toner For Development Of
Electrostatically Charged Image
Containing Polyolefin Resin
Having Cyclic Structure

Group Art Unit: 1756

Examiner: J. Dote

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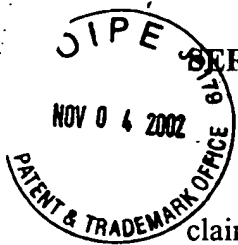
Commissioner for Patents
Washington, D.C. 20231

SUBMISSION OF ENGLISH CERTIFIED PRIORITY DOCUMENT

Sir:

In response to the Office Action of March 28, 2002, and the Amendment mailed September 30, 2002, the applicants enclose a certified English translation of their priority document (Japanese application no. 8-348 546 filed December 26, 1996). The applicants stated at page 10, of the Amendment mailed September 30, 2002 that they would submit the enclosed English Certified translation.

No additional fees are due. If there are any additional fees due in connection with the filing of this response, including any fees required for an additional extension of time under 37 CFR 1.136, such an extension is requested and the Commissioner is authorized to charge or credit any overpayment to Deposit Account No. 03-2775.



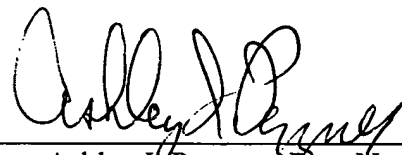
SERIAL NO. 09/331,29

ATTORNEY LOCKET NO. 1996/F 364

A prompt and favorable action is solicited. The applicants believe that these claims are in condition for allowance, however, if the Examiner disagrees, the applicants respectfully request that the Examiner telephone the undersigned at (302) 888-6270.

Respectfully submitted,

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RWS Group plc, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England, hereby declares that, to the best of its knowledge and belief, the following document, prepared by one of its translators competent in the art and conversant with the English and Japanese languages, is a true and correct translation of the accompanying document in the Japanese language.

Signed this 11th day of October 2002

S. ANTHONY

Director

For and on behalf of RWS Group plc



TRANSLATION FROM JAPANESE

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(19) Japan Patent Office (JP)

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Examined Claims: Unexamined Number of Claims: 6 OL (Total 19 Pages)

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(54) [Title of the Invention]

An Electrostatic Charge Image Developing Toner Containing a Cyclic Structure Polyolefin Resin

(57) [Summary]

[Problem] To provide a toner for electrostatic image development which has a wide non-offset temperature range sufficient for practical use and which can attain sufficient fixability even during high-speed copying.

[Resolution Means] In the developing toner, which consists essentially of a binder resin, a colorant, a functional additive, and a charge control agent, the binder resin comprises at least a cyclic structure polyolefin resin, said polyolefin resin being composed of a resin or resin fraction having a numeric average molecular weight (M_n), as measured by GPC, of less than 7,500, and a resin or resin fraction having a GPC numeric average molecular weight of 7,500 or more. The problem is resolved in that in the cyclic structure polyolefin resin, the resin or resin fraction is lower than 50 wt.% based on the whole binder resin, and has an intrinsic viscosity (i.v.) greater than or equal to 0.25 dl/g, a hot deformation temperature (HDT) of 70°C or more as determined by the DIN 53461-B method, a GPC numeric average molecular weight (M_n) of 7,500 or more, and a GPC weight-average molecular weight (M_w) of 15,000 or more.

[Scope of Patent Claims]

[Claim 1] A toner for development of an electrostatically charged image, said toner consisting essentially of a binder resin, a colorant, a function imparting agent, and a charge control agent, wherein said binder resin comprises at least a cyclic structure polyolefin resin, said cyclic structure polyolefin resin being composed of a resin or resin fraction having a numeric average molecular weight (M_n), as measured by GPC, of less than 7,500, and a resin or resin fraction having a GPC numeric average molecular weight of 7,500 or more, wherein in said cyclic structure polyolefin resin, said resin or resin fraction is lower than 50 wt.% based on the whole binder resin, and has an intrinsic viscosity (i.v.) greater than or equal to 0.25 dl/g, a hot deformation temperature (HDT) of 70°C or more as determined by the DIN 53461-B method, a GPC numeric average molecular weight (M_n) of 7,500 or more, and a GPC weight-average molecular weight (M_w) of 15,000 or more.

[Claim 2] The toner for development of an electrostatically charged image as claimed in claim 1, wherein said binder resin consists of 1 to 100 parts by weight of cyclic structure polyolefin resin, and 99 to 0 parts by weight of another resin comprising one of a polyester resin, an epoxy resin, a polyolefin resin, a vinyl acetate resin, a vinyl acetate copolymer resin, and a styrene-acrylate resin or other acrylate resin, or a mixture thereof.

[Claim 3] The toner for development of an electrostatically charged image as claimed in claim 1 or 2, wherein said cyclic structure polyolefin resin has at least one functional group selected from a carboxyl group, a hydroxyl group and an amino group.

[Claim 4] The toner for development of an electrostatically charged image as claimed in any one of claims 1 to 3, wherein said cyclic structure polyolefin resin comprises a cross-linked structure of an ionomer or a diene compound.

[Claim 5] The toner for development of an electrostatically charged image as claimed in any one of claims 1 to 4, wherein at least one type of wax, selected from amide wax, carnauba

wax, higher fatty acids and their esters, higher fatty acid metallic soaps, partially saponified higher fatty acid esters, higher aliphatic alcohols, polyolefin wax and paraffin wax, is used as said function imparting agent.

[Claim 6] The toner for development of an electrostatically charged image as claimed in any one of claims 1 to 5, wherein said cyclic structure polyolefin resin constituting said binder resin comprises resins or resin fractions having three molecular weight ranges, expressed by numeric average molecular weight (Mn) as measured by GPC, of less than 7,500, greater than or equal to 7,500 but less than 25,000, and greater than or equal to 2,5000.

[Detailed Description of the Invention]

[0001]

[Field of Utilization in Industry] The present invention relates to a toner for development of an electrostatically charged image. More specifically, this invention relates to a dry single-component magnetic toner, a dry single-component nonmagnetic toner, a dry dual-component toner, a dry polymerized toner, a liquid dried toner, or a liquid toner which, when fixed, is excellent for the prevention of spent toner, and which can form a well fixed, highly transparent and sharp image.

[0002] The invention also relates to the above-mentioned toner for use in copiers, printers, facsimile machines, color copiers, color laser copiers, color laser printers, and electro-photographic high speed printers.

[0003]

[Prior Art] Electrostatically charged image developing copiers and printers are gaining popularity because of widespread office automation. Against this background, demand is growing for high grade or sharp copied images which are highly light transmissive and well fixed. Under these circumstances, the following effect was stated by the present inventors in Japanese Patent Application No. Heisei 7-354063 (filed December 29, 1995), which was not laid open to the public when the present application was filed: "The relevant problem can be

solved or diminished by using a cyclic structure polyolefin resin as a binder resin for a toner, for heat roller fixing type electrostatically charged image developing copiers and printers, and also by incorporating less than 50% by weight of the abovementioned polyolefin resin, which has a high viscosity, into the entire binder resin. As a result, a sharp, high quality copied image excellent in fixing, light transmission and prevention of spent toner can be obtained. Such characteristics are exhibited particularly when this resin is used in a color toner."

[0004] This previous invention, however, was defective in that it was difficult to obtain a sufficiently broad non-offset temperature range suitable for practical use, and it failed to achieve full fixing at the higher copying speeds demanded by users. Further, although for fixing a toner image onto plain paper or onto an OHP film, various fixing methods are available, such as hot roller fixing, hot belt fixing, pressure fixing, radiant heat fixing, or flash fixing, in recent years, energy savings symbolized by Energy Star regulations have been increasingly called for, and demand has become intense for a toner fixable at low temperature and low pressure. The thermal and mechanical properties of conventional styrene-acrylate resins and polyester resins, or cyclic structure polyolefin resins, as described in Japanese Patent Application No. Heisei 7-354063, cannot satisfy beyond current levels the requirements for lower temperatures and pressures, and when the thermal properties of these resins are improved, deterioration of storage stability of the toner has resulted on the other hand.

[0005] General formulations for toners in electrostatically charged image developing copiers and printers are shown in Table 1.

(Table 1) General Toner Formulations

(Units : Weight %)

	Binder Resin	Colorant	Charge Control Agent	Function Imparting Agent	Magnetic Powder	Solvent
Dry Dual-Component Toner	50 - 100	0 - 20	0 - 10	0 - 20	--	--
Dry Non-Magnetic Single-Component Toner	50 - 100	0 - 20	0 - 10	0 - 20	--	--

Dry Magnetic Single-Component Toner	0 - 100	0 - 20	0 - 10	0 - 20	0 - 60	--
Dry Polymerized Toner	50 - 100	0 - 20	0 - 10	0 - 20		
Liquid Dried Toner	15 - 50	0 - 10	0 - 5	0 - 10	--	50 - 70
Liquid Toner	15 - 50	0 - 10	0 - 5	0 - 10	--	50 - 70

[0006]

[Problem to be Solved by the Invention] An object of the present invention is to provide a toner in a dry dual-component, dry nonmagnetic single-component, dry magnetic single-component, dry polymerized, liquid dried or liquid toner developer, and which exhibits the effects achieved by Japanese Patent Application No. Heisei 7-354063, wherein the toner exhibits a sufficiently broad non-offset temperature range suitable for practical use, can attain sufficient fixing even during high speed copying, and which provides a higher grade copied image, namely, a well fixed, highly optically transparent and sharp image, in an electrostatically charged image developing copier or printer.

[0007]

[Means for Solving the Problem] The foregoing object is attained by using, as a binder resin for the toner, a binder resin that comprises at least a cyclic structure polyolefin resin which cyclic structure polyolefin resin is composed of a resin or resin fraction having a numeric average molecular weight (Mn), as measured by GPC, of less than 7,500 and a resin or resin fraction having a GPC numeric average molecular weight of 7,500 or more. In the cyclic structure polyolefin resin, the resin or resin fraction is lower than 50 wt.% based on the whole binder resin, and has an intrinsic viscosity (i.v.) greater than or equal to 0.25 dl/g, a hot deformation temperature (HDT) of 70°C or more as determined by the DIN 53461-B method, a GPC numeric average molecular weight (Mn) of 7,500 or more, and a GPC weight-average molecular weight (Mw) of 15,000 or more.

[0008] Thus, the invention concerns a toner for development of an electrostatically charged image, the toner consisting essentially of a binder resin, a colorant, a function imparting agent

(generally, wax as a mold release agent), and a charge control agent, wherein said binder resin contains the abovementioned cyclic structure polyolefin resin, and the polyolefin resin satisfies the above conditions. The cyclic structure polyolefin resin used herein is, for example, a copolymer of an alpha-olefin (broadly, an acyclic olefin), such as ethylene, propylene or butylene, and an alicyclic compound (cycloolefin) having double bonds, such as cyclohexane or norbornene, the copolymer being colorless and transparent, and having high light transmissivity. The cyclic structure polyolefin resin is a polymer obtained, for example, by a polymerization method using a metallocene catalyst or a Ziegler catalyst.

[0009] Examples of synthesis of the cyclic structure polyolefin resin are disclosed in Japanese Laid-open Patent Application No. Heisei 5-339327, Japanese Laid-open Patent Application No. Heisei 5-9223, and Japanese Laid-open Patent Application No. Heisei 6-271628. According to these examples, the polyolefin resin is obtained by polymerizing one or more acyclic olefin monomers with one or more cycloolefin monomers at a temperature of -78 to 150°C, preferably 20 to 80°C, and a pressure of 0.01 to 64 bars, in the presence of a catalyst formed from at least one type of metallocene containing for example zirconium or hafnium together with a co-catalyst such as aluminoxane.

[0010] When dissolved in an inert hydrocarbon such as an aliphatic or aromatic hydrocarbon, the metallocene catalyst is activated. Thus, the metallocene catalyst is dissolved, for example, in toluene for preliminary activation and reaction in the solvent. During polymerization, the polymerization time and polymerization temperature must be adjusted, responding to conditions of the activity of the catalyst together with the desired molecular weight of the specific polymer block and desired molecular weight distribution.

[0011] The molar ratio of the acyclic olefin and the cycloolefin charged for the reaction can be varied widely depending on the targeted cyclic structure polyolefin resin. This ratio is adjusted, preferably, from 50:1 to 1:50, and more preferably from 20:1 to 1:20. Then, the copolymer components charged for the reaction are a total of two compounds, ethylene as the

acyclic polyolefin and norbornene as the cycloolefin, wherein the glass transition point (T_g) of the cyclic polyolefin resin, as a reaction product, is influenced greatly by their charge proportions. When the content of norbornene is increased, T_g also tends to rise. For example, when the proportion of norbornene charged is 10-15% by weight, T_g is about 60 to 70 °C.

[0012] Moreover, because the numeric average molecular weight of the cyclic structure polyolefin resin, and the characteristic value of intrinsic viscosity, change according to polymerization conditions such as reaction time and reaction temperature, the abovementioned resin having a desired numeric average molecular weight and desired limiting viscosity can be obtained. The colorless, transparent, and highly light-transmissive polyolefin having a cyclic structure, as used in the present invention, may be a mixture of a low-viscosity resin and a high-viscosity resin, wherein the low viscosity resin has a numeric average molecular weight, as measured by GPC, of less than 7,500, preferably 1,000 to less than 7,500, and more preferably 3,000 to less than 7,500, a weight average molecular weight, as measured by GPC, of less than 1,500, preferably 1,000 to less than 15,000, and more preferably 4,000 to less than 15,000, an i.v. (intrinsic viscosity) of less than 0.25 dl/g and an HDT (DIN-53461-B hot deformation temperature) of lower than 70°C, wherein the high-viscosity resin has a numeric average molecular weight, as measured by GPC, of 7,500 or more, preferably 7,500 to 50,000, a weight average molecular weight, as measured by GPC, of 15,000 or more, preferably 15,000 to 100,000, an i.v. of 0.25 dl/g or more and an HDT greater than or equal to 70°C. Alternatively, the polyolefin resin may have a molecular weight distribution with a single peak, containing a resin fraction having a numeric average molecular weight of less than 7,500 and a resin fraction having a numeric average molecular weight of 7,500 or more. Or alternatively, the polyolefin resin may have two or more peaks, in which its resin fraction having at least one of these peaks has a numeric average molecular weight of less than 7,500 and its resin fraction having the other peak has a numeric average molecular weight of 7,500 or more. The resin fractions mentioned here refer to respective

resin components before mixing, if the cyclic structure polyolefin resin is composed of a mixture of different components, such as those with various numeric average molecular weights, or otherwise refer to resin divisions formed by fractionating the final synthetic product by a suitable means such as GPC. If the resin fractions are monodispersed or close to being monodispersed, an M_n of 7,500 nearly corresponds to an M_w of 15,000.

[0013] The high and low viscosity cyclic structure polyolefin resins have the above-mentioned numeric average molecular weights M_n , weight average molecular weights M_w , intrinsic viscosities i.v. and hot deformation temperatures (HDT). Thus, the M_w/M_n ratio, used as a measure of the degree of dispersion of the molecular weight distribution, may be as low as from 1 to 2.5, or more specifically, is in a monodispersed or nearly monodispersed state. Thus, a toner having a quick heat response and a high fixing strength can be produced. Such a polyolefin resin not only enables fixing at a low temperature and a low pressure, but also contributes to the storage stability, prevention of spent toner, and electric stability properties such as uniform charge distribution, constant charging efficiency or static elimination efficiency. If the low viscosity resin, in particular, is monodispersed or nearly monodispersed, the resulting toner exhibits improved heat response characteristics, such as an instantaneous melting or setting behavior.

[0014] The abovementioned high and low viscosity cyclic structure polyolefin resin, moreover, is colorless, transparent, and highly light-transmissive. For instance, when the azo-pigment Permanent Rubin F6B (produced by Hoechst Inc.) was added to the resin, and the mixture thoroughly kneaded and then formed into a sheet by means of a press, the sheet was confirmed to be highly transparent. Thus, the resin is sufficiently usable as a color toner. Measurement by the DSC method has shown this polyolefin resin to require a very low heat of fusion, and thus the resin can be expected to markedly reduce energy consumption during fixing.

[0015] The high-viscosity cyclic structure polyolefin resin also has the abovementioned

physical properties. Thus, compared to the same low-viscosity polyolefin resin, it imparts a structural viscosity to the toner, thereby improving the offset preventing effect, as well as its adhesion to a copying medium such as paper or film. However, if the amount of said high-viscosity resin used is 50% by weight or more, based on the entire binder resin, uniform kneading properties thereof decline dramatically, impeding toner performance. In other words, a high grade image, i.e., a sharp image with high fixing strength and excellent heat response, cannot be obtained.

[0016] The toner for development of an electrostatically charged image according to the present invention comprises a binder resin that contains at least cyclic structure polyolefin resin, and moreover, by using the abovementioned polyolefin resins having both low viscosity and high viscosity as described above, the non-offset temperature range thereof encompasses both high temperature and the low temperature sides, fixing properties during high speed copying are enhanced, and fixing properties at both low temperatures and low pressures are improved.

[0017] The abovementioned low viscosity polyolefin resin with a numeric average molecular weight of less than 7,500 contributes to broadening the non-offset temperature range on the low temperature side. On the other hand, the abovementioned high viscosity polyolefin resin with a numeric average molecular weight of 7,500 or more contributes to broadening the non-offset temperature range on the high temperature side. In order to broaden the non-offset temperature range on the high temperature side more effectively, it is preferable to use an abovementioned high viscosity polyolefin resin with a numeric average molecular weight of 20,000 or more. Proportions of the cyclic structure polyolefin resins having numeric average molecular weights of less than 7,500 and 7,500 or more, contained in the entire binder resin, are each preferably 0.5 parts by weight or more, and more preferably 5 parts by weight or more, based on 100 parts by weight of the entire binder resin. If the content of each polyolefin resin is less than 0.5 parts by weight, it is difficult to obtain a practical broad offset

temperature range.

[0018] Moreover, in the case of a cyclic structure polyolefin resin composed of the abovementioned low viscosity polyolefin resin having a numeric average molecular weight of less than 7,500 and the abovementioned high viscosity polyolefin resin having a numeric average molecular weight of 25,000 or more, a medium viscosity cyclic structure polyolefin resin having a numeric average molecular weight of 7,500 or more, but less than 25,000, may be added to enhance compatibility between the low and high viscosity resin components. Such an additive has been found effective for continuously bringing about the non-offset range.

[0019] In other words, in the binder resin containing at least a cyclic structure polyolefin resin, if the polyolefin resin comprises resins or resin fractions having three molecular weight ranges expressed by numeric average molecular weights (M_n) as measured by GPC, respectively, of less than 7,500, 7,500 or more but less than 25,000, and 25,000 or more, an advantageous embodiment of the present invention is also provided. The resin fractions constituting the abovementioned respective molecular weight ranges may be comprise resins having a molecular weight distribution with one or two peaks, which can be divided into fractions with the three molecular weight ranges expressed as M_n . Alternatively, the resin fractions constituting the respective molecular weight ranges may constitute a mixture of resins having molecular weight distributions with three or more peaks and having at least one molecular weight peak in each of the abovementioned molecular weight ranges.

[0020] The proportion of the medium viscosity polyolefin resin or resin fraction is preferably 1 part by weight or more, and more preferably 5 parts by weight or more, based on 100 parts by weight of the entire binder resin, in order to increase compatibility. In the present invention, a toner using as the binder resin a mixture of polyolefin resins, composed of both resins or resin fractions with an M_n of less than 7,500 and an M_n of 7,500 or more, together with another resin, also realizes a high grade image, i.e., a sharp image with high fixing

strength. The other resin refers to one of a polyester resin, an epoxy resin, a polyolefin resin, a vinyl acetate type resin, a vinyl acetate type copolymer resin, a styrene-acrylic resin or other acrylic type resins, or mixtures thereof. In this case, the proportions of the cyclic structure polyolefin resin and other resin used in the binder resin are 1 to 100, preferably 20 to 90, more preferably 50 to 90 parts by weight of the former, and 99 to 0, preferably 80 to 10, more preferably 50 to 10 parts by weight of the latter. If the amount of the former resin is less than 1 part by weight, it becomes difficult to obtain a high grade image.

[0021] By introducing carboxyl groups into the cyclic structure polyolefin resin, compatibility with the other resin and dispersibility of the pigment can be improved. Furthermore, adhesion to paper or film, which serves as the copying medium, can be enhanced, leading to increased fixability. However, if an acrylic-acid type monomer is mixed with acyclic olefins and cycloolefins when carrying out polymerization of said resin, then polymerization cannot be carried out due to a decrease in activity of the metallocene catalyst. Therefore, a two-stage reaction method, comprising polymerization of the cyclic structure polyolefin resin first, and subsequently introducing carboxyl groups, is preferred.

[0022] Generally speaking there are two methods available for introducing carboxyl groups into said resin. One method is to oxidize an alkyl group, such as a methyl group, at the terminal of the resin, using a fusing air oxidation method, to convert it into a carboxyl group. With this method, however, the cyclic structure polyolefin resin that has been synthesized using a metallocene catalyst has barely any branches, making it difficult to introduce many carboxyl groups into said resin. Another method is to add a peroxide to said resin, and react maleic anhydride with the resulting radical portion. Using this method, it is theoretically possible to introduce many carboxyl groups into said resin, however, overly increasing the proportion of introduced carboxyl groups results in yellowing of said resin, making its transparency poor. If the use of the product is restricted to a toner, therefore, it is preferred to introduce 1 to 15% by weight of maleic anhydride, based on resin. If the maleic anhydride is

introduced at a weight ratio of less than 1%, then no effect occurs with respect to compatibility with other resins nor with respect to dispersibility of the pigment. Moreover, when the amount of introduced maleic anhydride exceeds 15%, bridging formations between molecules are easily generated, greatly increasing the molecular weight, so that the kneading characteristics and gridability of the resin make it no longer suitable for practical use. The same improvement can be achieved by introducing hydroxyl groups or amino groups using known methods.

[0023] Further, to improve fixability of the toner, a cross-linked structure may be introduced into the cyclic structure polyolefin resin. One method for introducing such a cross-linked structure is to add a diene monomer, such as norbornadiene or cyclohexadiene, together with the acyclic olefins and the cycloolefins, followed by reacting the system, to thereby obtain a ternarypolymeric polyolefin having a cyclic structure. As a result of this method, said resin acquires termini exhibiting activity even without a cross-linking agent. Known chemical reactions, such as oxidation or epoxidation, or the addition of cross-linking agents to form a cross-linked structure, results in the resin functioning in this manner.

[0024] Another method is to add a metal such as zinc, copper or calcium to the cyclic structure polyolefin resin, which also has carboxyl groups introduced therein, and then blend and melt the mixture with a screw or the like, to disperse the metal uniformly as fine particles within the resin, and imparting a cross-linked structure by forming an ionomer. Concerning a technology on such an ionomer, United States Patent No. 4,693,941, for example, discloses an ethylene terpolymer containing carboxyl groups which take the form of a divalent metal salt upon partial or complete neutralization, in an attempt to obtain toughening thereof. For the same purpose, PCT (WO) 6-500348 reports a polyester resin molded product containing an ionomer of an unsaturated carboxylic acid that has about 20 to 80% of the carboxylic acid groups thereof neutralized with zinc, cobalt, nickel, aluminum or copper (II).

[0025] The toner of the present invention uses a known function imparting agent to enhance

offset prevention. To improve this performance further, the addition of wax has been found effective. At least one wax selected from amide wax, carnauba wax, higher fatty acids and their esters, higher fatty acid metallic soaps, partially saponified higher fatty acid esters, and higher aliphatic alcohols can be used as a polar wax for the function imparting agent. At least one wax selected from polyolefin wax and paraffin wax can be used as a non-polar wax for the function imparting agent.

[0026] More specifically, it is thought that the polar wax functions as an external lubricant for the abovementioned polyolefin resin, a nonpolar resin, because of the difference in polarity thereof and that the nonpolar polyolefin wax etc. function as an external lubricant mainly because of the ease of surface migration, due to the low molecular weight, contributing to an improved non-offset characteristic. The toner for development of an electrostatically charged image according to the present invention is also obtainable by adding a colorant, a charge control agent, a function imparting agent, and if desired, other additives to the abovementioned binder resin, while using known methods such as extrusion, kneading, grinding and classification, and a plasticizer, lubricant or the like, may further be added.

[0027] A known colorant may be used, such as carbon black, diazo yellow, phthalocyanine blue, quinacridone, carmine 6B, monoazo red or perylene. A known charge control agent may be used, such as Nigrosine dyes, fatty acid modified Nigrosine dyes, metallized Nigrosine dyes, metallized fatty acid modified Nigrosine dyes, chromium complexes of 3,5-di-tert-butylsalicylic acid, quaternary ammonium salts, triphenylmethane dyes, and azochromium complexes.

[0028] A flowing agent such as colloidal silica, aluminum oxide or titanium oxide, and a lubricant comprising a fatty acid metal salt such as barium stearate, calcium stearate or barium laurate, may further be added to the toner of the present invention. The toner of the present invention can be used as a dry single-component magnetic toner, a dry single-

component nonmagnetic toner, a dry dual-component toner, a dry polymerized toner, a liquid dried toner, or a liquid toner. The invention is applicable to copiers, printers, facsimile machines and electro-photographic high speed printers. The invention is further applicable as a full-color toner in color copiers, color laser copiers and color laser printers.

[0029]

[Working Examples] The present invention will be described in more detail with reference to working examples and comparative examples. The physical properties of the cyclic structure polyolefin resin, used in the present invention, are measured by the following methods:

GPC Conditions for Measurement of Molecular Weight

Molecular weight conversion method: Standard polyethylene used

Column used: JORDI-SAEULE 500x10 LINEAR

Mobile phase: 1,2-dichlorobenzene (135°C) (flow rate 0.5 ml/mm)

Detector: Differential Refractometer

Method for measurement of intrinsic viscosity: Inherent viscosity at 135°C, when
0.5 g of the resin was uniformly dissolved in 100 ml of decalin

Toner preparation method 1

Dry nonmagnetic single-component system and dry dual-component system: 1% by weight of a charge control agent (Copy Charge NX, manufactured by Hoechst), 4% by weight of amide wax (BNT, manufactured by Nippon Seika), 0.5% by weight of aerosol silica (HDK-H2000, manufactured by Wacker Chemie), 5% by weight of magenta pigment (Permanent Rubin F6B, manufactured by Hoechst) as a colorant, and 89.5% by weight of a binder resin were mixed and melt kneaded at 130°C using twin rollers. Then, the mixture was cooled to solidification and coarsely crushed, followed by finely dividing the particles using a jet mill. The resulting fine particles were classified to select particles with an average particle diameter of about 10 μm , thereby preparing the toner.

[0030] Toner preparation method 2

Dry magnetic single-component system: 40% by weight of a magnetic powder (BL100, Titanium Industry), 1% by weight of a charge control agent (Copy Charge NX, manufactured by Hoechst), 4% by weight of wax (BNT, manufactured by Nippon Seika), 0.5% by weight of aerosol silica (HDK-H2000, manufactured by Wacker Chemie), 2.0% by weight of calcium carbonate (manufactured by Shiraishi Calcium) as an extender pigment and a structural viscosity improver, and 52.5% by weight of a binder resin were mixed and melt kneaded at 150°C using twin rollers. Then, the mixture was cooled to coagulation and coarsely ground, followed by finely dividing the particles using a jet mill. The resulting fine particles were classified to select particles with an average particle diameter of about 10 μm , thereby preparing the toner.

[0031] Toner preparation method 3

Dry polymerized system: 1% by weight of a charge control agent (Copy Charge NX, manufactured by Hoechst), 4% by weight of wax (BNT, manufactured by Nippon Seika), 0.5% by weight of aerosol silica (HDK-H2000, manufactured by Wacker Chemie), and 5% by weight of magenta pigment (Permanent Rubin F6B, manufactured by Hoechst) as a colorant were mechanically dispersed and mixed in monomer components corresponding to 89.5% by weight of a binder resin during polymerization of the binder resin. The mixture was interfacially polymerized into particles with an average particle diameter of about 10 μm , thereby preparing the toner.

[0032] Toner preparation method 4

Liquid dried system: 40% by weight of the toner, obtained using the formulation of the dry polymerized system, and 60% by weight of an electrolytic solution (Isopar H, manufactured by Exxon) were mixed, and kneaded by a sand mill to prepare the toner.

Toner preparation method 5

Liquid toner: 40% by weight of a mixture consisting of 1 part by weight of carbon black (MA-7, manufactured by Mitsubishi Chemical Corp.) as a colorant, 0.5 part by weight of a

charge control agent (Reflex Blue R51, manufactured by Hoechst), and 98.5 parts by weight of a binder resin was mixed with 60% by weight of an electrolytic solution (Isopar H, manufactured by Exxon). The mixture was kneaded with a sand mill to prepare a toner.

[0033]

Table 1

Working Example or Comparative Example No.	Toner Preparation Method	Formulation of Binder Resin			
		Sample No.	Weight %	Sample No.	Weight %
Working Ex. 1	1 and 3	1	89.5	--	--
Working Ex. 2	1 and 3	1	60	2	29.5
Working Ex. 3	1 and 3	1	60	7	29.5
Working Ex. 4	1 and 3	3	89.5	--	--
Working Ex. 5	1 and 3	3	60	7	29.5
Working Ex. 6	1 and 3	5	89.5	--	--
Working Ex. 7	1 and 3	5	60	7	29.5
Working Ex. 8	1 and 3	1	60	2	14.5
				9	15
Working Ex. 9	2	1	52.5	--	--
Working Ex. 10	2	1	30	2	22.5
Working Ex. 11	2	1	30	7	22.5
Working Ex. 12	2	1	30	8	22.5
Working Ex. 13	2	3	52.5	--	--
Working Ex. 14	2	3	30	7	22.5
Working Ex. 15	2	3	30	8	22.5
Working Ex. 16	2	5	52.5	--	--
Working Ex. 17	2	5	30	7	22.5
Working Ex. 18	2	5	30	8	22.5
Working Ex. 19	2	1	30	2	11
	2			9	11.5
Working Ex. 20	4 and 5	1	39.4	--	--
Working Ex. 21	4 and 5	1	24	2	15.4
Working Ex. 22	4 and 5	1	24	7	15.4
Working Ex. 23	4 and 5	1	24	8	15.4
Working Ex. 24	4 and 5	3	39.4	--	--
Working Ex. 25	4 and 5	3	24	7	15.4
Working Ex. 26	4 and 5	3	24	8	15.4
Working Ex. 27	4 and 5	5	39.4	--	--
Working Ex. 28	4 and 5	5	24	7	15.4
Working Ex. 29	4 and 5	5	24	8	15.4
Working Ex. 30	4 and 5	1	24	2	7.4
				9	8
Comparative Ex. 1	1 and 3	7	89.5	--	--
Comparative Ex. 2	1 and 3	8	89.5	--	--
Comparative Ex. 3	2	7	52.5	--	--
Comparative Ex. 4	2	8	52.5	--	--
Comparative Ex. 5	4 and 5	7	39.4	--	--
Comparative Ex. 6	4 and 5	8	39.4	--	--

Table 2 shows the fundamental properties of the cyclic structure polyolefin resin used in the present invention.

[0034]

Table 2 : Fundamental Properties

Sample No.	Name	Mw	Mn	i.v.	HDT	Mw/Mn	Tg
1	MT 845	6250	3350	0.19	<70	1.9	61
2	MT 854	66100	27700	1.39	<70	2.4	66
3	T-745'-MO	6800	3400	<0.25	<70	2.0	78
5	T-745'-CL	12000	3900	<0.25	<70	3.5	76
7	Tafton NE 2155: Polyester Resin, Kao Corp.						
8	MC 100: Styrene Acrylic Resin, Nippon Carbide Industries						
9	MT 849	40100	22200	0.7	≥70	1.8	65
10	T-745	7000	3800	0.19	<70	1.8	68

Tg: Glass transition point

Sample No. 1 (MT845), No. 2 (MT854) and No. 9 (MT849) are cyclic structure polyolefin resins having a low viscosity, a high viscosity and a medium viscosity, respectively.

[0035] Sample No. 3 (T-745' -MO): Prepared by reacting Sample No. 10 (T-745), a binary copolymer of ethylene and norbornene, with a peroxide and 7% by weight, based on T- 745, of maleic anhydride, to introduce carboxyl groups therein.

Sample No. 5 (T-745' -CL): Prepared by neutralizing about 70% of the carboxyl groups of Sample No. 3 (T-745' -MO), which has carboxyl groups introduced therein, with zinc for conversion into an ionomer.

[0036] Tafton NE 2155: Tg = 65°C MC100: Tg = 69°C, Mw = 53000, Mn = 23000, Mw/Mn = 2.3

The toners prepared by the abovementioned toner preparation methods 1, 2 and 3 were each placed in a commercially available electro-photographic copier (PC100, manufactured by Canon Inc.) and subjected to performance testing. Then, the toners prepared by toner

preparation methods 4 and 5 were each placed in a commercially available electro-photographic copier (FT400i, manufactured by Ricoh Co., Ltd.) and subjected to performance testing. The results are shown in Table 3.

[0037]

Table 3

	Fixability 10 copies/min	Image Sharpness		Light Transmission 624 nm	Spent Toner Characteristic	Non-Offset Characteristic
		Thin Line Resolving Power	Gray Scale			
Working Ex. 1	○	○	○	○	○	△
Working Ex. 2	○	○	○	○	○	○
Working Ex. 3	○	△	△	△	△	△
Working Ex. 4	◎	○	○	○	○	△
Working Ex. 5	◎	○	○	○	○	△
Working Ex. 6	◎	○	○	○	○	○
Working Ex. 7	◎	△	△	△	△	○
Working Ex. 8	◎	○	○	○	○	◎
Working Ex. 9	○	○	○	—	○	△
Working Ex. 10	○	○	○	—	○	○
Working Ex. 11	○	○	○	—	△	△
Working Ex. 12	○	○	○	—	△	△
Working Ex. 13	◎	○	○	—	○	△
Working Ex. 14	◎	○	○	—	○	△
Working Ex. 15	◎	○	○	—	○	△
Working Ex. 16	◎	○	○	—	○	○
Working Ex. 17	◎	○	○	—	△	○
Working Ex. 18	◎	○	○	—	△	○
Working Ex. 19	◎	○	○	○	○	◎
Working Ex. 20	○	○	○	—	○	△
Working Ex. 21	○	○	○	—	○	○
Working Ex. 22	○	○	○	—	—	△
Working Ex. 23	○	○	○	—	—	△
Working Ex. 24	◎	○	○	—	—	△
Working Ex. 25	◎	○	○	—	—	△
Working Ex. 26	◎	○	○	—	—	△

Working Ex. 27	◎	○	○	—	—	○
Working Ex. 28	◎	○	○	—	—	○
Working Ex. 29	◎	○	○	—	—	○
Working Ex. 30	◎	○	○	○	○	◎
Comp. Ex. 1	×	△	△	○	×	×
Comp. Ex. 2	×	×	×	×	×	×
Comp. Ex. 3	×	○	○	—	×	×
Comp. Ex. 4	×	○	○	—	×	×
Comp. Ex. 5	×	○	○	—	×	×
Comp. Ex. 6	×	○	○	—	×	×

In Working Examples 1 to 8 and 20 to 30, and Comparative Examples 1, 2, 5 and 6, two methods for toner preparation are employed. However, the toner composition and resin matrix are common, so the evaluation results for these items are the same.

[0038] Evaluation Methods and Assessment Criteria

1) Fixability

The toners prepared according to the respective formulations were each used for copying onto recycled paper at a copying rate of 10 copies/min at a fixing temperature of 110 to 140°C, wherein the fixing temperature for each copying cycle was raised by 10°C. The resulting copy samples were rubbed 10 times with an eraser using an abrasion tester manufactured by Sutherland Co. The load during the test was 40 g/cm². The tested samples were measured for printing density using a Macbeth type reflection densitometer. The symbol × was assigned when even one of the measured values at the respective temperatures was less than 65%, the symbol △ was assigned when the measured values at the respective temperatures were 65% or more but less than 75%, the symbol ○ was assigned when the measured values at the respective temperatures were 75% or more but less than 85%, and the symbol ◎ was assigned when the measured values at the respective temperatures were 85% or more.

[0039] 2) Image Sharpness

Toners prepared according to the respective formulations were each used for copying onto recycled paper. The resulting samples were checked against sample images manufactured by Data Quest. The thin line resolving power and gray scale of the copy image were used as bases for evaluation. The symbol \times was assigned for a thin line resolving power of 200 dots/inch or less, \triangle for a thin line resolving power of 201 to 300 dots/inch, and \bigcirc for a thin line resolving power of 301 dots/inch or more. The ratio of the reflection density of the copy image to the reflection density of the sample image, at each step of the gray scale, was evaluated as \times when less than 65%, \triangle when 65% or more but less than 75%, and \bigcirc when 75% or more.

[0040] 3) Light Transmission

Magenta-colored toners prepared according to the formulations of the working examples and comparative examples were each used to produce sheet-shaped samples with a film thickness of 100 μm . Light transmission of each sheet sample was measured using a spectral filter having a peak at 624 nm. The light transmittance at 624 nm was evaluated as \times when less than 8%, \triangle when 8% or more but less than 11%, and \bigcirc when 11% or more.

[0041] 4) Spent Toner Resistance

Toners described in each of the embodiments the comparative examples were placed in predetermined amounts into a developer box, together a ferrite carrier manufactured by Powdertech. After the mixture was agitated and triboelectrically treated for 1 week, 5 g of the toner-deposited carrier was weighed. Such a toner-deposited carrier was placed in soapy water to remove the toner electrostatically adhering to the surface. Only the carrier magnetic powder was withdrawn using a magnet. The magnetic powder was immersed in acetone to dissolve and remove spent toner fused to the surface. The change in weight after immersion was compared with the weight before immersion, and was evaluated as \bigcirc when less than 0.2%, \triangle when 0.2% or more but less than 0.5%, and \times when 0.5% or more.

[0042] 5) Non-Offset Characteristic

Toners prepared according the respective formulations were each used for copying onto recycled paper at a copying rate of 10 copies/min and at a fixing temperature of 90 to 180°C, wherein the fixing temperature for each copying cycle was raised by 10°C. The printing density of the non-image areas of the resulting samples was measured using a Macbeth type reflection densitometer. A printing density of 0.2 or less (printing density of paper = 0.15) represented a non-offset state. The difference between the upper limit and lower limit temperatures in the non-offset state was evaluated as × when 0°C, △ when 1 to 20°C, ○ when 21 to 40°C, and ⊙ when higher than 40°C.

[Procedural Amendment]

[Date of Submission] February 7, 1997

[Procedural Amendment 1]

[Name of Document to be Amended] Specification

[Name of Item to be Amended] All

[Method of Amendment] Alteration

[Document Name] Specification

[Title of Invention] An Electrostatic Charge Image Developing Toner Containing a Cyclic Structure Polyolefin Resin

[Scope of Patent Claims]

[Claim 1] A toner for development of an electrostatically charged image, said toner consisting essentially of a binder resin, a colorant, a function imparting agent, and a charge control agent, wherein said binder resin comprises at least a cyclic structure polyolefin resin, said cyclic structure polyolefin resin being composed of a resin or resin fraction having a numeric average molecular weight (M_n), as measured by GPC, of less than 7,500, and a resin or resin fraction having a GPC numeric average molecular weight of 7,500 or more, wherein in said cyclic structure polyolefin resin, said resin or resin fraction is lower than 50 wt.% based on the whole binder resin, and has an intrinsic viscosity (i.v.) greater than or equal to 0.25 dl/g, a hot deformation temperature (HDT) of 70°C or more as determined by the DIN 53461-B method, a GPC numeric average molecular weight (M_n) of 7,500 or more, and a GPC weight-average molecular weight (M_w) of 15,000 or more.

[Claim 2] The toner for development of an electrostatically charged image as claimed in claim 1, wherein said binder resin consists of 1 to 100 parts by weight of cyclic structure polyolefin resin, and 99 to 0 parts by weight of another resin comprising one of a polyester resin, an epoxy resin, a polyolefin resin, a vinyl acetate resin, a vinyl acetate copolymer resin, and a styrene-acrylate resin or other acrylate resin, or a mixture thereof.

[Claim 3] The toner for development of an electrostatically charged image as claimed in claim 1 or 2, wherein said cyclic structure polyolefin resin has at least one functional group selected from a carboxyl group, a hydroxyl group and an amino group.

[Claim 4] The toner for development of an electrostatically charged image as claimed in any one of claims 1 to 3, wherein said cyclic structure polyolefin resin comprises a cross-linked structure of an ionomer or a diene compound.

[Claim 5] The toner for development of an electrostatically charged image as claimed in any one of claims 1 to 4, wherein at least one type of wax, selected from amide wax, carnauba wax, higher fatty acids and their esters, higher fatty acid metallic soaps, partially saponified

higher fatty acid esters, higher aliphatic alcohols, polyolefin wax and paraffin wax, is used as said function imparting agent.

[Claim 6] The toner for development of an electrostatically charged image as claimed in any one of claims 1 to 5, wherein said cyclic structure polyolefin resin constituting said binder resin comprises resins or resin fractions having three molecular weight ranges, expressed by numeric average molecular weight (Mn) as measured by GPC, of less than 7,500, greater than or equal to 7,500 but less than 25,000, and greater than or equal to 2,5000.

[Detailed Description of the Invention]

[0001]

[Field of Utilization in Industry] The present invention relates to a toner for development of an electrostatically charged image. More specifically, this invention relates to a dry single-component magnetic toner, a dry single-component nonmagnetic toner, a dry dual-component toner, a dry polymerized toner, a liquid dried toner, or a liquid toner which, when fixed, is excellent for the prevention of spent toner, and which can form a well fixed, highly transparent and sharp image.

[0002] The invention also relates to the above-mentioned toner for use in copiers, printers, facsimile machines, color copiers, color laser copiers, color laser printers, and electro-photographic high speed printers.

[0003]

[Prior Art] Electrostatically charged image developing copiers and printers are gaining popularity because of widespread office automation. Against this background, demand is growing for high grade or sharp copied images which are highly light transmissive and well fixed. Under these circumstances, the following effect was stated by the present inventors in Japanese Patent Application No. Heisei 7-354063 (filed December 29, 1995), which was not laid open to the public when the present application was filed: "The relevant problem can be solved or diminished by using a cyclic structure polyolefin resin as a binder resin for a toner,

for heat roller fixing type electrostatically charged image developing copiers and printers, and also by incorporating less than 50% by weight of the abovementioned polyolefin resin, which has a high viscosity, into the entire binder resin. As a result, a sharp, high quality copied image excellent in fixing, light transmission and prevention of spent toner can be obtained. Such characteristics are exhibited particularly when this resin is used in a color toner."

[0004] This previous invention, however, was defective in that it was difficult to obtain a sufficiently broad non-offset temperature range suitable for practical use, and it failed to achieve full fixing at the higher copying speeds demanded by users. Further, although for fixing a toner image onto plain paper or onto an OHP film, various fixing methods are available, such as hot roller fixing, hot belt fixing, pressure fixing, radiant heat fixing, or flash fixing, in recent years, energy savings symbolized by Energy Star regulations have been increasingly called for, and demand has become intense for a toner fixable at low temperature and low pressure. The thermal and mechanical properties of conventional styrene-acrylate resins and polyester resins, or cyclic structure polyolefin resins, as described in Japanese Patent Application No. Heisei 7-354063, cannot satisfy beyond current levels the requirements for lower temperatures and pressures, and when the thermal properties of these resins are improved, deterioration of storage stability of the toner has resulted on the other hand.

[0005] General formulations for toners in electrostatically charged image developing copiers and printers are shown in Table 1.

(Table 1) General Toner Formulations

(Units : Weight %)

	Binder Resin	Colorant	Charge Control Agent	Function Imparting Agent	Magnetic Powder	Solvent
Dry Dual-Component Toner	50 - 100	0 - 20	0 - 10	0 - 20	--	--
Dry Non-Magnetic Single-Component Toner	50 - 100	0 - 20	0 - 10	0 - 20	--	--
Dry Magnetic Single-Component Toner	0 - 100	0 - 20	0 - 10	0 - 20	0 - 60	--

Dry Polymerized Toner	50 - 100	0 - 20	0 - 10	0 - 20		
Liquid Dried Toner	15 - 50	0 - 10	0 - 5	0 - 10	--	50 - 70
Liquid Toner	15 - 50	0 - 10	0 - 5	0 - 10	--	50 - 70

[0006]

[Problem to be Solved by the Invention] An object of the present invention is to provide a toner in a dry dual-component, dry nonmagnetic single-component, dry magnetic single-component, dry polymerized, liquid dried or liquid toner developer, and which exhibits the effects achieved by Japanese Patent Application No. Heisei 7-354063, wherein the toner exhibits a sufficiently broad non-offset temperature range suitable for practical use, can attain sufficient fixing even during high speed copying, and which provides a higher grade copied image, namely, a well fixed, highly optically transparent and sharp image, in an electrostatically charged image developing copier or printer.

[0007]

[Means for Solving the Problem] The foregoing object is attained by using, as a binder resin for the toner, a binder resin that comprises at least a cyclic structure polyolefin resin which cyclic structure polyolefin resin is composed of a resin or resin fraction having a numeric average molecular weight (Mn), as measured by GPC, of less than 7,500 and a resin or resin fraction having a GPC numeric average molecular weight of 7,500 or more. In the cyclic structure polyolefin resin, the resin or resin fraction is lower than 50 wt.% based on the whole binder resin, and has an intrinsic viscosity (i.v.) greater than or equal to 0.25 dl/g, a hot deformation temperature (HDT) of 70°C or more as determined by the DIN 53461-B method, a GPC numeric average molecular weight (Mn) of 7,500 or more, and a GPC weight-average molecular weight (Mw) of 15,000 or more.

[0008] Thus, the invention concerns a toner for development of an electrostatically charged image, the toner consisting essentially of a binder resin, a colorant, a function imparting agent (generally, wax as a mold release agent), and a charge control agent, wherein said binder resin

contains the abovementioned cyclic structure polyolefin resin, and the polyolefin resin satisfies the above conditions. The cyclic structure polyolefin resin used herein is, for example, a copolymer of an alpha-olefin (broadly, an acyclic olefin), such as ethylene, propylene or butylene, and an alicyclic compound (cycloolefin) having double bonds, such as cyclohexane or norbornene, the copolymer being colorless and transparent, and having high light transmissivity. The cyclic structure polyolefin resin is a polymer obtained, for example, by a polymerization method using a metallocene catalyst or a Ziegler catalyst.

[0009] Examples of synthesis of the cyclic structure polyolefin resin are disclosed in Japanese Laid-open Patent Application No. Heisei 5-339327, Japanese Laid-open Patent Application No. Heisei 5-9223, and Japanese Laid-open Patent Application No. Heisei 6-271628. According to these examples, the polyolefin resin is obtained by polymerizing one or more acyclic olefin monomers with one or more cycloolefin monomers at a temperature of -78 to 150°C, preferably 20 to 80°C, and a pressure of 0.01 to 64 bars, in the presence of a catalyst formed from at least one type of metallocene containing for example zirconium or hafnium together with a co-catalyst such as aluminoxane.

[0010] When dissolved in an inert hydrocarbon such as an aliphatic or aromatic hydrocarbon, the metallocene catalyst is activated. Thus, the metallocene catalyst is dissolved, for example, in toluene for preliminary activation and reaction in the solvent. During polymerization, the polymerization time and polymerization temperature must be adjusted, responding to conditions of the activity of the catalyst together with the desired molecular weight of the specific polymer block and desired molecular weight distribution.

[0011] The molar ratio of the acyclic olefin and the cycloolefin charged for the reaction can be varied widely depending on the targeted cyclic structure polyolefin resin. This ratio is adjusted, preferably, from 50:1 to 1:50, and more preferably from 20:1 to 1:20. Then, the copolymer components charged for the reaction are a total of two compounds, ethylene as the acyclic polyolefin and norbornene as the cycloolefin, wherein the glass transition point (Tg)

of the cyclic polyolefin resin, as a reaction product, is influenced greatly by their charge proportions. When the content of norbornene is increased, Tg also tends to rise. For example, when the proportion of norbornene charged is 10-15% by weight, Tg is about 60 to 70°C.

[0012] Moreover, because the numeric average molecular weight of the cyclic structure polyolefin resin, and the characteristic value of intrinsic viscosity, change according to polymerization conditions such as reaction time and reaction temperature, the abovementioned resin having a desired numeric average molecular weight and desired limiting viscosity can be obtained. The colorless, transparent, and highly light-transmissive polyolefin having a cyclic structure, as used in the present invention, may be a mixture of a low-viscosity resin and a high-viscosity resin, wherein the low viscosity resin has a numeric average molecular weight, as measured by GPC, of less than 7,500, preferably 1,000 to less than 7,500, and more preferably 3,000 to less than 7,500, a weight average molecular weight, as measured by GPC, of less than 15,000, preferably 1,000 to less than 15,000, and more preferably 4,000 to less than 15,000, an i.v. (intrinsic viscosity) of less than 0.25 dl/g and an HDT (DIN-53461-B hot deformation temperature) of lower than 70°C, wherein the high-viscosity resin has a numeric average molecular weight, as measured by GPC, of 7,500 or more, preferably 7,500 to 50,000, a weight average molecular weight, as measured by GPC, of 15,000 or more, preferably 15,000 to 100,000, an i.v. of 0.25 dl/g or more and an HDT greater than or equal to 70°C. Alternatively, the polyolefin resin may have a molecular weight distribution with a single peak, containing a resin fraction having a numeric average molecular weight of less than 7,500 and a resin fraction having a numeric average molecular weight of 7,500 or more. Or alternatively, the polyolefin resin may have two or more peaks, in which its resin fraction having at least one of these peaks has a numeric average molecular weight of less than 7,500 and its resin fraction having the other peak has a numeric average molecular weight of 7,500 or more. The resin fractions mentioned here refer to respective resin components before mixing, if the cyclic structure polyolefin resin is composed of a

mixture of different components, such as those with various numeric average molecular weights, or otherwise refer to resin divisions formed by fractionating the final synthetic product by a suitable means such as GPC. If the resin fractions are monodispersed or close to being monodispersed, an M_n of 7,500 nearly corresponds to an M_w of 15,000.

[0013] The high and low viscosity cyclic structure polyolefin resins have the above-mentioned numeric average molecular weights M_n , weight average molecular weights M_w , intrinsic viscosities i.v. and hot deformation temperatures (HDT). Thus, the M_w/M_n ratio, used as a measure of the degree of dispersion of the molecular weight distribution, may be as low as from 1 to 2.5, or more specifically, is in a monodispersed or nearly monodispersed state. Thus, a toner having a quick heat response and a high fixing strength can be produced. Such a polyolefin resin not only enables fixing at a low temperature and a low pressure, but also contributes to the storage stability, prevention of spent toner, and electric stability properties such as uniform charge distribution, constant charging efficiency or static elimination efficiency. If the low viscosity resin, in particular, is monodispersed or nearly monodispersed, the resulting toner exhibits improved heat response characteristics, such as an instantaneous melting or setting behavior.

[0014] The abovementioned high and low viscosity cyclic structure polyolefin resin, moreover, is colorless, transparent, and highly light-transmissive. For instance, when the azo-pigment Permanent Rubin F6B (produced by Hoechst Inc.) was added to the resin, and the mixture thoroughly kneaded and then formed into a sheet by means of a press, the sheet was confirmed to be highly transparent. Thus, the resin is sufficiently usable as a color toner. Measurement by the DSC method has shown this polyolefin resin to require a very low heat of fusion, and thus the resin can be expected to markedly reduce energy consumption during fixing.

[0015] The high-viscosity cyclic structure polyolefin resin also has the abovementioned physical properties. Thus, compared to the same low-viscosity polyolefin resin, it imparts a

structural viscosity to the toner, thereby improving the offset preventing effect, as well as its adhesion to a copying medium such as paper or film. However, if the amount of said high-viscosity resin used is 50% by weight or more, based on the entire binder resin, uniform kneading properties thereof decline dramatically, impeding toner performance. In other words, a high grade image, i.e., a sharp image with high fixing strength and excellent heat response, cannot be obtained.

[0016] The toner for development of an electrostatically charged image according to the present invention comprises a binder resin that contains at least cyclic structure polyolefin resin, and moreover, by using the abovementioned polyolefin resins having both low viscosity and high viscosity as described above, the non-offset temperature range thereof encompasses both high temperature and the low temperature sides, fixing properties during high speed copying are enhanced, and fixing properties at both low temperatures and low pressures are improved.

[0017] The abovementioned low viscosity polyolefin resin with a numeric average molecular weight of less than 7,500 contributes to broadening the non-offset temperature range on the low temperature side. On the other hand, the abovementioned high viscosity polyolefin resin with a numeric average molecular weight of 7,500 or more contributes to broadening the non-offset temperature range on the high temperature side. In order to broaden the non-offset temperature range on the high temperature side more effectively, it is preferable to use an abovementioned high viscosity polyolefin resin with a numeric average molecular weight of 20,000 or more. Proportions of the cyclic structure polyolefin resins having numeric average molecular weights of less than 7,500 and 7,500 or more, contained in the entire binder resin, are each preferably 0.5 parts by weight or more, and more preferably 5 parts by weight or more, based on 100 parts by weight of the entire binder resin. If the content of each polyolefin resin is less than 0.5 parts by weight, it is difficult to obtain a practical broad offset temperature range.

[0018] Moreover, in the case of a cyclic structure polyolefin resin composed of the abovementioned low viscosity polyolefin resin having a numeric average molecular weight of less than 7,500 and the abovementioned high viscosity polyolefin resin having a numeric average molecular weight of 25,000 or more, a medium viscosity cyclic structure polyolefin resin having a numeric average molecular weight of 7,500 or more, but less than 25,000, may be added to enhance compatibility between the low and high viscosity resin components. Such an additive has been found effective for continuously bringing about the non-offset range.

[0019] In other words, in the binder resin containing at least a cyclic structure polyolefin resin, if the polyolefin resin comprises resins or resin fractions having three molecular weight ranges expressed by numeric average molecular weights (M_n) as measured by GPC, respectively, of less than 7,500, 7,500 or more but less than 25,000, and 25,000 or more, an advantageous embodiment of the present invention is also provided. The resin fractions constituting the abovementioned respective molecular weight ranges may be comprise resins having a molecular weight distribution with one or two peaks, which can be divided into fractions with the three molecular weight ranges expressed as M_n . Alternatively, the resin fractions constituting the respective molecular weight ranges may constitute a mixture of resins having molecular weight distributions with three or more peaks and having at least one molecular weight peak in each of the abovementioned molecular weight ranges.

[0020] The proportion of the medium viscosity polyolefin resin or resin fraction is preferably 1 part by weight or more, and more preferably 5 parts by weight or more, based on 100 parts by weight of the entire binder resin, in order to increase compatibility. In the present invention, a toner using as the binder resin a mixture of polyolefin resins, composed of both resins or resin fractions with an M_n of less than 7,500 and an M_n of 7,500 or more, together with another resin, also realizes a high grade image, i.e., a sharp image with high fixing strength. The other resin refers to one of a polyester resin, an epoxy resin, a polyolefin type

resin, a vinyl acetate type resin, a vinyl acetate type copolymer resin, a styrene-acrylic resin or other acrylic type resins, or mixtures thereof. In this case, the proportions of the cyclic structure polyolefin resin and other resin used in the binder resin, in the case of 100 parts by weight of the binder resin, are 1 to 100, preferably 20 to 90, more preferably 50 to 90 parts by weight of the former, and 99 to 0, preferably 80 to 10, more preferably 50 to 10 parts by weight of the latter. If the amount of the former resin is less than 1 part by weight, it becomes difficult to obtain a high grade image.

[0021] By introducing carboxyl groups into the cyclic structure polyolefin resin, compatibility with the other resin and dispersibility of the pigment can be improved. Furthermore, adhesion to paper or film, which serves as the copying medium, can be enhanced, leading to increased fixability. However, if an acrylic-acid type monomer is mixed with acyclic olefins and cycloolefins when carrying out polymerization of said resin, then polymerization cannot be carried out due to a decrease in activity of the metallocene catalyst. Therefore, a two-stage reaction method, comprising polymerization of the cyclic structure polyolefin resin first, and subsequently introducing carboxyl groups, is preferred.

[0022] Generally speaking there are two methods available for introducing carboxyl groups into said resin. One method is to oxidize an alkyl group, such as a methyl group, at the terminal of the resin, using a fusing air oxidation method, to convert it into a carboxyl group. With this method, however, the cyclic structure polyolefin resin that has been synthesized using a metallocene catalyst has barely any branches, making it difficult to introduce many carboxyl groups into said resin. Another method is to add a peroxide to said resin, and react maleic anhydride with the resulting radical portion. Using this method, it is theoretically possible to introduce many carboxyl groups into said resin, however, overly increasing the proportion of introduced carboxyl groups results in yellowing of the resin, making its transparency poor. If the use of the product is restricted to a toner, therefore, it is preferred to introduce 1 to 15% by weight of maleic anhydride, based on said resin. If the maleic

anhydride is introduced at a weight ratio of less than 1%, then no effect occurs with respect to compatibility with other resins nor with respect to dispersibility of the pigment. Moreover, when the amount of introduced maleic anhydride exceeds 15%, bridging formations between molecules are easily generated, greatly increasing the molecular weight, so that the kneading characteristics and gridability of the resin make it no longer suitable for practical use. The same improvement can be achieved by introducing hydroxyl groups or amino groups using known methods.

[0023] Further, to improve fixability of the toner, a cross-linked structure may be introduced into the cyclic structure polyolefin resin. One method for introducing such a cross-linked structure is to add a diene monomer, such as norbornadiene or cyclohexadiene, together with the acyclic olefins and the cycloolefins, followed by reacting the system, to thereby obtain a ternarypolymeric polyolefin having a cyclic structure. As a result of this method, said resin acquires termini exhibiting activity even without a cross-linking agent. Known chemical reactions, such as oxidation or epoxidation, or the addition of cross-linking agents to form a cross-linked structure, results in the resin functioning in this manner.

[0024] Another method is to add a metal such as zinc, copper or calcium to the cyclic structure polyolefin resin, which also has carboxyl groups introduced therein, and then blend and melt the mixture with a screw or the like, to disperse the metal uniformly as fine particles within the resin, and imparting a cross-linked structure by forming an ionomer. Concerning a technology on such an ionomer, United States Patent No. 4,693,941, for example, discloses an ethylene terpolymer containing carboxyl groups which take the form of a divalent metal salt upon partial or complete neutralization, in an attempt to obtain toughening thereof. For the same purpose, PCT (WO) 6-500348 reports a polyester resin molded product containing an ionomer of an unsaturated carboxylic acid that has about 20 to 80% of the carboxylic acid groups thereof neutralized with zinc, cobalt, nickel, aluminum or copper (II).

[0025] The toner of the present invention uses a known function imparting agent to enhance

offset prevention. To improve this performance further, the addition of wax has been found effective. At least one wax selected from amide wax, carnauba wax, higher fatty acids and their esters, higher fatty acid metallic soaps, partially saponified higher fatty acid esters, and higher aliphatic alcohols can be used as a polar wax for the function imparting agent. At least one wax selected from polyolefin wax and paraffin wax can be used as a non-polar wax for the function imparting agent.

[0026] More specifically, it is thought that the polar wax functions as an external lubricant for the abovementioned polyolefin resin, a nonpolar resin, because of the difference in polarity thereof and that the nonpolar polyolefin wax etc. function as an external lubricant mainly because of the ease of surface migration, due to the low molecular weight, contributing to an improved non-offset characteristic. The toner for development of an electrostatically charged image according to the present invention is also obtainable by adding a colorant, a charge control agent, a function imparting agent, and if desired, other additives to the abovementioned binder resin, while using known methods such as extrusion, kneading, grinding and classification, and a plasticizer, lubricant or the like, may further be added.

[0027] A known colorant may be used, such as carbon black, diazo yellow, phthalocyanine blue, quinacridone, carmine 6B, monoazo red or perylene. A known charge control agent may be used, such as Nigrosine dyes, fatty acid modified Nigrosine dyes, metallized Nigrosine dyes, metallized fatty acid modified Nigrosine dyes, chromium complexes of 3,5-di-tert-butylsalicylic acid, quaternary ammonium salts, triphenylmethane dyes, and azochromium complexes.

[0028] A flowing agent such as colloidal silica, aluminum oxide or titanium oxide, and a lubricant comprising a fatty acid metal salt such as barium stearate, calcium stearate or barium laurate, may further be added to the toner of the present invention. The toner of the present invention can be used as a dry single-component magnetic toner, a dry single-

component nonmagnetic toner, a dry dual-component toner, a dry polymerized toner, a liquid dried toner, or a liquid toner. The invention is applicable to copiers, printers, facsimile machines and electro-photographic high speed printers. The invention is further applicable as a full-color toner in color copiers, color laser copiers and color laser printers.

[0029]

[Working Examples] The present invention will be described in more detail with reference to working examples and comparative examples. The physical properties of the cyclic structure polyolefin resin, used in the present invention, are measured by the following methods:

GPC Conditions for Measurement of Molecular Weight

Molecular weight conversion method: Standard polyethylene used

Column used: JORDI-SAEULE 500x10 LINEAR

Mobile phase: 1,2-dichlorobenzene (135 °C) (flow rate 0.5 ml/mm)

Detector: Differential Refractometer

Method for measurement of intrinsic viscosity: Inherent viscosity at 135°C, when

0.5 g of the resin was uniformly dissolved in 100 ml of decalin

Toner preparation method 1

Dry nonmagnetic single-component system and dry dual-component system: 1% by weight of a charge control agent (Copy Charge NX, manufactured by Hoechst), 4% by weight of amide wax (BNT, manufactured by Nippon Seika), 0.5% by weight of aerosol silica (HDK-H2000, manufactured by Wacker Chemie), 5% by weight of magenta pigment (Permanent Rubin F6B, manufactured by Hoechst) as a colorant, and 89.5% by weight of a binder resin were mixed and melt kneaded at 130°C using twin rollers. Then, the mixture was cooled to solidification and coarsely crushed, followed by finely dividing the particles using a jet mill. The resulting fine particles were classified to select particles with an average particle diameter of about 10 μm , thereby preparing the toner.

[0030] Toner preparation method 2

Dry magnetic single-component system: 40% by weight of a magnetic powder (BL100, Titanium Industry), 1% by weight of a charge control agent (Copy Charge NX, manufactured by Hoechst), 4% by weight of wax (BNT, manufactured by Nippon Seika), 0.5% by weight of aerosol silica (HDK-H2000, manufactured by Wacker Chemie), 2.0% by weight of calcium carbonate (manufactured by Shiraishi Calcium) as an extender pigment and a structural viscosity improver, and 52.5% by weight of a binder resin were mixed and melt kneaded at 150°C using twin rollers. Then, the mixture was cooled to coagulation and coarsely ground, followed by finely dividing the particles using a jet mill. The resulting fine particles were classified to select particles with an average particle diameter of about 10 μm , thereby preparing the toner.

[0031] Toner preparation method 3

Dry polymerized system: 1% by weight of a charge control agent (Copy Charge NX, manufactured by Hoechst), 4% by weight of wax (BNT, manufactured by Nippon Seika), 0.5% by weight of aerosol silica (HDK-H2000, manufactured by Wacker Chemie), and 5% by weight of magenta pigment (Permanent Rubin F6B, manufactured by Hoechst) as a colorant were mechanically dispersed and mixed in monomer components corresponding to 89.5% by weight of a binder resin during polymerization of the binder resin. The mixture was interfacially polymerized into particles with an average particle diameter of about 10 μm , thereby preparing the toner.

[0032] Toner preparation method 4

Liquid dried system: 40% by weight of the toner, obtained using the formulation of the dry polymerized system, and 60% by weight of an electrolytic solution (Isopar H, manufactured by Exxon) were mixed, and kneaded by a sand mill to prepare the toner.

Toner preparation method 5

Liquid toner: 40% by weight of a mixture consisting of 1 part by weight of carbon black (MA-7, manufactured by Mitsubishi Chemical Corp.) as a colorant, 0.5 part by weight of a

charge control agent (Reflex Blue R51, manufactured by Hoechst), and 98.5 parts by weight of a binder resin was mixed with 60% by weight of an electrolytic solution (Isopar H, manufactured by Exxon). The mixture was kneaded with a sand mill to prepare a toner.

[0033]

Table 1

Working Example or Comparative Example No.	Toner Preparation Method	Formulation of Binder Resin			
		Sample No.	Weight %	Sample No.	Weight %
Working Ex. 1	1 and 3	1	89.5	--	--
Working Ex. 2	1 and 3	1	60	2	29.5
Working Ex. 3	1 and 3	1	60	7	29.5
Working Ex. 4	1 and 3	3	60	--	--
Working Ex. 5	1 and 3	3	89.5	7	29.5
Working Ex. 6	1 and 3	5	60	--	--
Working Ex. 7	1 and 3	5	60	7	29.5
Working Ex. 8	1 and 3	1	60	2	14.5
				9	15
Working Ex. 9	2	1	52.5	--	--
Working Ex. 10	2	1	30	2	22.5
Working Ex. 11	2	1	30	7	22.5
Working Ex. 12	2	1	30	8	22.5
Working Ex. 13	2	3	52.5	--	--
Working Ex. 14	2	3	30	7	22.5
Working Ex. 15	2	3	30	8	22.5
Working Ex. 16	2	5	52.5	--	--
Working Ex. 17	2	5	30	7	22.5
Working Ex. 18	2	5	30	8	22.5
Working Ex. 19	2	1	30	2	11
	2			9	11.5
Working Ex. 20	4 and 5	1	39.5	--	--
Working Ex. 21	4 and 5	1	24	2	15.4
Working Ex. 22	4 and 5	1	24	7	15.4
Working Ex. 23	4 and 5	1	24	8	15.4
Working Ex. 24	4 and 5	3	39.4	--	--
Working Ex. 25	4 and 5	3	24	7	15.4
Working Ex. 26	4 and 5	3	24	8	15.4
Working Ex. 27	4 and 5	5	39.4	--	--
Working Ex. 28	4 and 5	5	24	7	15.4
Working Ex. 29	4 and 5	5	24	8	15.4
Working Ex. 30	4 and 5	1	24	2	7.4
				9	8
Comparative Ex. 1	1 and 3	7	89.5	--	--
Comparative Ex. 2	1 and 3	8	89.5	--	--
Comparative Ex. 3	2	7	52.5	--	--
Comparative Ex. 4		8	52.5	--	--
Comparative Ex. 5	4 and 5	7	39.4	--	--
Comparative Ex. 6	4 and 5	8	39.4	--	--

Table 2 shows the fundamental properties of the cyclic structure polyolefin resin used in the present invention.

[0034]

Table 2 : Fundamental Properties

Sample No.	Name	Mw	Mn	i.v.	HDT	Mw/Mn	Tg
1	MT 845	6250	3350	0.19	<70	1.9	61
2	MT 854	66100	27700	1.39	<70	2.4	66
3	T-745'-MO	6800	3400	<0.25	<70	2.0	78
5	T-745'-CL	12000	3900	<0.25	<70	3.5	76
7	Tafton NE 2155: Polyester Resin, Kao Corp.						
8	MC 100: Styrene Acrylic Resin, Nippon Carbide Industries						
9	MT 849	40100	22200	0.7	≥70	1.8	65
10	T-745	7000	3800	0.19	<70	1.8	68

Tg: Glass transition point

Sample No. 1 (MT845), No. 2 (MT854) and No. 9 (MT849) are cyclic structure polyolefin resins having a low viscosity, a high viscosity and a medium viscosity, respectively.

[0035] Sample No. 3 (T-745' -MO): Prepared by reacting Sample No. 10 (T-745), a binary copolymer of ethylene and norbornene, with a peroxide and 7% by weight, based on T- 745, of maleic anhydride, to introduce carboxyl groups therein.

Sample No. 5 (T-745' -CL): Prepared by neutralizing about 70% of the carboxyl groups of Sample No. 3 (T-745' -MO), which has carboxyl groups introduced therein, with zinc for conversion into an ionomer.

[0036] Tafton NE 2155: Tg = 65°C MC100: Tg = 69°C, Mw = 53000, Mn = 23000, Mw/Mn = 2.3

The toners prepared by the abovementioned toner preparation methods 1, 2 and 3 were each placed in a commercially available electro-photographic copier (PC100, manufactured by Canon Inc.) and subjected to performance testing. Then, the toners prepared by toner

preparation methods 4 and 5 were each placed in a commercially available electro-
photographic copier (FT400i, manufactured by Ricoh Co., Ltd.) and subjected to
performance testing. The results are shown in Table 3.

[0037]

Table 3

	Fixability 10 copies/min	Image Sharpness		Light Transmission 624 nm	Spent Toner Characteristic	Non-Offset Characteristic
		Thin Line Resolving Power	Gray Scale			
Working Ex. 1	○	○	○	○	○	△
Working Ex. 2	○	○	○	○	○	○
Working Ex. 3	○	△	△	△	△	△
Working Ex. 4	◎	○	○	○	○	△
Working Ex. 5	◎	○	○	○	○	△
Working Ex. 6	◎	○	○	○	○	○
Working Ex. 7	◎	△	△	△	△	○
Working Ex. 8	◎	○	○	○	○	◎
Working Ex. 9	○	○	○	—	○	△
Working Ex. 10	○	○	○	—	○	○
Working Ex. 11	○	○	○	—	△	△
Working Ex. 12	○	○	○	—	△	△
Working Ex. 13	◎	○	○	—	○	△
Working Ex. 14	◎	○	○	—	○	△
Working Ex. 15	◎	○	○	—	○	△
Working Ex. 16	◎	○	○	—	○	○
Working Ex. 17	◎	○	○	—	△	○
Working Ex. 18	◎	○	○	—	△	○
Working Ex. 19	◎	○	○	○	○	◎
Working Ex. 20	○	○	○	—	○	△
Working Ex. 21	○	○	○	—	○	○
Working Ex. 22	○	○	○	—	—	△
Working Ex. 23	○	○	○	—	—	△
Working Ex. 24	◎	○	○	—	—	△
Working Ex. 25	◎	○	○	—	—	△
Working Ex. 26	◎	○	○	—	—	△

Working Ex. 27	◎	○	○	—	—	○
Working Ex. 28	◎	○	○	—	—	○
Working Ex. 29	◎	○	○	—	—	○
Working Ex. 30	◎	○	○	○	○	◎
Comp. Ex. 1	×	△	△	○	×	×
Comp. Ex. 2	×	×	×	×	×	×
Comp. Ex. 3	×	○	○	—	×	×
Comp. Ex. 4	×	○	○	—	×	×
Comp. Ex. 5	×	○	○	—	×	×
Comp. Ex. 6	×	○	○	—	×	×

In Working Examples 1 to 8 and 20 to 30, and Comparative Examples 1, 2, 5 and 6, two methods for toner preparation are employed. However, the toner composition and resin matrix are common, so the evaluation results for these items are the same.

[0038] Evaluation Methods and Assessment Criteria

1) Fixability

The toners prepared according to the respective formulations were each used for copying onto recycled paper at a copying rate of 10 copies/min at a fixing temperature of 110 to 140°C, wherein the fixing temperature for each copying cycle was raised by 10°C. The resulting copy samples were rubbed 10 times with an eraser using an abrasion tester manufactured by Sutherland Co. The load during the test was 40 g/cm². The tested samples were measured for printing density using a Macbeth type reflection densitometer. The symbol × was assigned when even one of the measured values at the respective temperatures was less than 65%, the symbol △ was assigned when the measured values at the respective temperatures were 65% or more but less than 75%, the symbol ○ was assigned when the measured values at the respective temperatures were 75% or more but less than 85%, and the symbol ◎ was assigned when the measured values at the respective temperatures were 85% or more.

[0039] 2) Image Sharpness

Toners prepared according to the respective formulations were each used for copying onto recycled paper. The resulting samples were checked against sample images manufactured by Data Quest. The thin line resolving power and gray scale of the copy image were used as bases for evaluation. The symbol \times was assigned for a thin line resolving power of 200 dots/inch or less, \triangle for a thin line resolving power of 201 to 300 dots/inch, and \bigcirc for a thin line resolving power of 301 dots/inch or more. The ratio of the reflection density of the copy image to the reflection density of the sample image, at each step of the gray scale, was evaluated as \times when less than 65%, \triangle when 65% or more but less than 75%, and \bigcirc when 75% or more.

[0040] 3) Light Transmission

Magenta-colored toners prepared according to the formulations of the working examples and comparative examples were each used to produce sheet-shaped samples with a film thickness of 100 μm . Light transmission of each sheet sample was measured using a spectral filter having a peak at 624 nm. The light transmittance at 624 nm was evaluated as \times when less than 8%, \triangle when 8% or more but less than 11%, and \bigcirc when 11% or more.

[0041] 4) Spent Toner Resistance

Toners described in each of the embodiments the comparative examples were placed in predetermined amounts into a developer box, together a ferrite carrier manufactured by Powdertech. After the mixture was agitated and triboelectrically treated for 1 week, 5 g of the toner-deposited carrier was weighed. Such a toner-deposited carrier was placed in soapy water to remove the toner electrostatically adhering to the surface. Only the carrier magnetic powder was withdrawn using a magnet. The magnetic powder was immersed in acetone to dissolve and remove spent toner fused to the surface. The change in weight after immersion was compared with the weight before immersion, and was evaluated as \bigcirc when less than 0.2%, \triangle when 0.2% or more but less than 0.5%, and \times when 0.5% or more.

[0042] 5) Non-Offset Characteristic

Toners prepared according the respective formulations were each used for copying onto recycled paper at a copying rate of 10 copies/min and at a fixing temperature of 90 to 180°C, wherein the fixing temperature for each copying cycle was raised by 10°C. The printing density of the non-image areas of the resulting samples was measured using a Macbeth type reflection densitometer. A printing density of 0.2 or less (printing density of paper = 0.15) represented a non-offset state. The difference between the upper limit and lower limit temperatures in the non-offset state was evaluated as × when 0°C, △ when 1 to 20°C, ○ when 21 to 40°C, and ◎ when higher than 40°C.

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F Terms (Reference)	2H005	AA01	AA06	AA08	AA21	CA02
		CA04	CA07	CA08	CA13	CA14
		CA17	CB07	CB13	DA04	DA06
		DA10	EA03	EA06	EA07	FA01
		FA06	FA07			